Abstract

Nanoparticles exhibit in comparison to their bulk material modified magnetic properties and peculiar magnetic phenomena, such as superparamagnetism. The magnetic properties of nanoparticles are hereby defined by the finite size, increased surface-to-volume ratio, shape, dipolar and the exchange interactions. All these effects have different impacts on the underlying spin structure and are not fully understood and in-depth elucidated. In the scope of this thesis, the impact of different effects on the nanoparticle magnetic properties is studied for four different types of magnetic nanoparticles: cobalt ferrite ($CoFe_2O_4$), wüstite-ferrite core-shell ($FeO@CoFe_2O_4$), cobalt chromite ($CoCr_2O_4$) nanospheres and hematite ($\alpha-Fe_2O_3$) nanospindles. The magnetic nanoparticles are mainly investigated by the combination of X-ray and neutron scattering as well as diffraction methods accompanied by transmission electron microscopy, macroscopic magnetization measurements and Mössbauer spectroscopy.

Surface effects are evaluated for single phase $CoFe_2O_4$. The intraparticle magnetization distribution is elucidated using polarized small-angle neutron scattering (SANSPOL), which provides the necessary nm-resolution. The magnetic morphology is analyzed using a spherical magnetic form factor, where the magnetic radius is allowed to be smaller than the nuclear particle radius. The obtained results reveal a variation of the coherently magnetized volume with applied magnetic field, and allow to estimate the energy needed to polarize the disordered spin at the nanoparticle surface. Spin-resolved small-angle scattering (POLARIS) gives unique access to the transversal magnetization components, which allows to distinguish between – theoretically proposed – correlated and – in this work – found disordered, non-correlated spins at the nanoparticle surface.

Matrix effects in magnetic heterostructures are addressed for the example of $FeO@CoFe_2O_4$ core-shell NPs. The challenging characterization of the chemical composition and magnetic morphology on the nm length scale is fully achieved using the advantage of the different sensitivities of neutron and X-ray small-angle scattering. The magnetization distribution in the weakly ferrimagnetic wüstite-like core and the strongly ferrimagnetic spinel shell of the core-shell nanoparticles is resolved using half-polarized small-angle neutron scattering. The slow, continuous oxidation of the Fe^{2+} ions present in the wüstite-like structure of the core is tracked over several years giving a hint to improve the synthesis towards single-phase spherical nanoparticles.

The orientation of nanoparticles is studied in-depth for hematite spindles, where the magnetocrystalline anisotropy overcomes the shape anisotropy and decisively influences the orientation behavior of the nanoparticles, which align perpendicularly to the applied magnetic field. Simultaneous field-dependent small-angle and wide-angle X-ray scattering give access to the morphological and crystallographic orientation of the hematite nanospindles. The morphological orientation is fully described by a ellipsoid rotating around the magnetic easy axis confined in the equatorial plane, while the inclination angle between the magnetic field and the easy axis is described by a Langevin behavior. The magnetic easy axis is fixed in the basal plane coinciding with the particle short axis of the hematite spindle. However strong thermal fluctuations of the particle moment within the hematite basal plane is found.

The effect of size, *inter*- and *intra*particle interactions are investigated for $CoCr_2O_4$

nanocrystals with different batches covering the size range of 2.7 - 21.9 nm. The change of the magnetic transitions from paramagnetic to superparamagnetic and from superparamagnetic to ferrimagnetic order are evaluated using vibrating sample magnetometry. Polarized neutron diffraction with XYZ polarization analysis allow to determine the spin-spiral transition temperature, where additional magnetic satellite reflections appear in the magnetic scattering. The results allow to construct the size-dependent magnetic phase diagram and to reveal the critical particle diameters for the non-collinear and collinear magnetic ordering. It will be shown that for nanocrystallite size as small as 3 nm, *intra*particle interactions lead to a magnetic frustrated state of the nanoparticle.

In view of biomedical application, a improved ligand exchange synthesis will be presented for transferring magnetic nanoparticles from non-polar media into polar solvents such as water, which does not affect the particle size, size distribution and without formation of aggregates.